

NISTIR 6242

ANNUAL CONFERENCE ON FIRE RESEARCH
Book of Abstracts
November 2-5, 1998

Kellie Ann Beall, Editor

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EXTINCTION OF HYDROFLUOROCARBON FLAMES WITH F/H RATIOS OF UNITY AND GREATER¹

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Hydrofluorocarbons (HFCs) are being considered as replacements for chlorofluorocarbon (CFC) refrigerants because HFCs do not deplete stratospheric ozone when released to the atmosphere. In general, the exchange of a halogen atom in a molecule with hydrogen decreases the atmospheric lifetime of the compound. It may also increase the efficiency of the refrigeration machine. Both of these effects are highly desirable from environmental considerations since they act to mitigate global warming; however, more hydrogen on an HFC is usually associated with an increase in flammability. An accepted method for determining the flammability limits of gaseous fuels is ASTM Standard E 681. The minimum and maximum concentrations of the fuel in air for flame propagation are based upon the observed ignition and growth of a flame in a vessel filled with a quiescent fuel/air mixture. A clear distinction is sought between a non-propagating flicker and a flame which has enough horizontal propagation to be hazardous. When applied to hydrocarbons, these tests give well-defined results. Fuels with fluorine-to-carbon ratios approaching unity have a great sensitivity to the test conditions and provide ambiguous limits due to vagaries in the ignition source, to vessel geometry complexities, and to operator subjectivity.

Many of the difficulties associated with the ASTM apparatus are not present in a premixed, counter-flow burner. With this apparatus, steady flames first are established under favorable conditions, and then the fraction of fuel is diminished in small increments until the flame is extinguished. The tests are repeated at progressively lower flow rates, which are inherently more capable of sustaining combustion. By plotting the fraction of fuel at extinction versus the flow rate and extrapolating to an experimentally unattainable zero-flow condition, an unambiguous limit of flammability can be attained. Unlike the ASTM apparatus, the counter-flow burner method entirely avoids issues surrounding the design of an ignition mechanism, it minimizes heat loss and wall effects, and also it is amenable to computational analysis.

HFC flame studies are typically carried out in mixtures with hydrocarbons, in which the overall H-atom concentration is considerably greater than the F-atom. As the F/H ratio approaches unity, the flame speed decreases substantially, making it difficult to stabilize even lightly stretched stoichiometric flames. The HFCs investigated in this study [CH_2F_2 (R-32), C_2HF_5 (R-125) and $\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$ (R-245ca)] have F/H ratios equal to or greater than one. The pure CH_2F_2 /air flame can be established over a range of equivalence ratios and stretch rates. Figure 1 shows the limiting mole fraction of CH_2F_2 in air for which a flame can be sustained for a given global stretch rate (defined as the mean burner nozzle velocity divided by the distance from the outlet to the stagnation plane). The open diamonds and circles represent dry initial conditions, and the filled symbols are data taken with the air humidified to a dew point of about 12 °C. The solid line is the best fit through the humid data for an initial mixture temperature of 100 °C. The dotted line corresponds to a fit of dry conditions for a nominal initial temperature between 25 °C and 35 °C. Extrapolating the straight lines to the vertical axis yields a mole fraction that is equivalent to a lower flammability limit for CH_2F_2 /air mixtures. Increasing the temperature decreases the limiting mole fraction of CH_2F_2 from 0.14 ± 0.004 at 30 °C to 0.13 ± 0.004 at 100 °C; changing the relative humidity has no statistical significance.

A flame of C_2HF_5 and air can not be stabilized under any condition. Hence, R-125 is properly classified as non-flammable. By mixing the C_2HF_5 with CH_2F_2 , a critical mole fraction of R-125 in the refrigerant mixture can be reached which just renders it non-flammable. Figure 2 shows how increasing the fraction of R-125 decreases the stretch rate necessary to extinguish the flame, as a function of equivalence ratio. The equivalence ratio that leads to the highest extinguishing stretch rate lies between 1.15 and 1.25, with higher mole fractions of C_2HF_5 pushing the peak closer the stoichiometric condition. Note that both

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refrigerants are treated as fuels when computing the equivalence ratio since equilibrium calculations indicate that, at flame temperatures, the main products are HF, COF_2 , CF_4 , and CO_2 . The critical flammability ratio (CFR), defined as the minimum mole fraction of R-125 in the refrigerant mixture required to prevent flame propagation under any conditions, can be estimated by extrapolating the peak extinction stretch rate versus R-125 mole fraction curve to a zero-stretch condition. Using this technique, a CFR of 0.18 ± 0.004 is found for dry air initially at $30^\circ\text{C} \pm 5^\circ\text{C}$. For experiments performed at 100°C and humidified to a dew point of 12°C , a greater mole fraction of R-125 was required to extinguish the flame at each stretch rate, increasing the CFR to 0.22 ± 0.004 for these conditions.

Pure $\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$ with air does not produce a stable flame under the conditions examined in the counter flow burner. It does burn easily when supplemented with CH_2F_2 , and it is possible to decrease the amount of CH_2F_2 needed for a flame as the stretch rate is decreased. Extrapolating to a zero mole fraction of CH_2F_2 suggests that a flame might exist if the initial temperature is 100°C and dew point is 12°C for a narrow range of equivalence ratios around 1.3, as long as the stretch rate is below 6 s^{-1} . Flames with such low stretch rates can not be maintained in the presence of normal buoyant forces. If the water vapor is removed from the air, or if the temperature is reduced to 50°C , no flammable range can be obtained for a finite value of stretch rate.

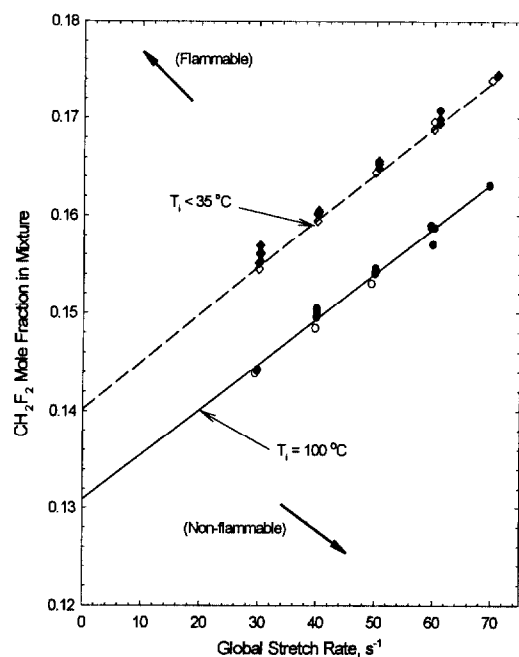


Figure 1. Extinction mole fraction of CH_2F_2 /air mixtures as a function of flame stretch, showing impact of initial temperature and humidity. Solid symbols: $T_{\text{dew pt}} = 12^\circ\text{C}$; open symbols: dry air.

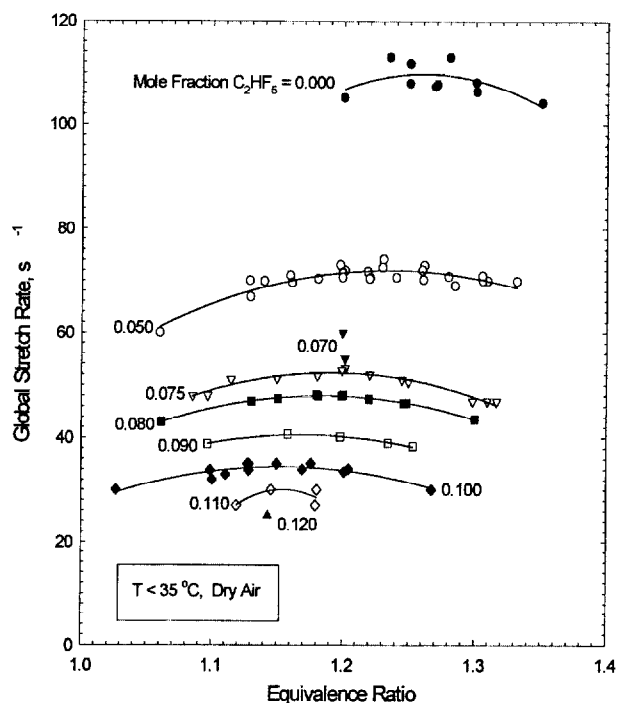


Figure 2. Extinction stretch rates for fixed values of C_2HF_5 mole fraction in fuel mixture, as a function of total equivalence ratio.